



DECLARATION

I, Atsuko SANABE, translator of the attached document, do hereby certify that to the best of my knowledge and belief the attached document is the true English translation of Japanese Patent Application No. 2002-365782 duly filed with the Japan Patent Office as of December 17, 2002.

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 [Title of the Invention] Toner for Developing
 Electrostatic Latent Image,
 Developer and Fixing Method
 [Scope of Claims]

[Claim 1]

Toner, used for developing an electrostatic latent image, obtained in such a manner that:

toner particles comprising: a binder resin including a modified polyester resin being capable of reacting with active hydrogen, and a low molecular resin with a weight average molecular weight of from 2,000 to 10,000; a colorant; and a release agent; are dissolved or dispersed in an organic solvent, to be made into particles as well as subjected to a polymerization reaction in an aqueous medium, and the solvent is obtained from the solution by methods including removing, cleaning and drying,

wherein the binder resin has a glass transition temperature of from 35°C to below 55 °C, and fine particles with an average diameter of from 0.002 to 0.2 times that of the toner particles are embedded in the surface of toner.

[Claim 2]

Toner used for developing an electrostatic latent image as described in claim 1, wherein the fine particle includes a particulate resin having a glass transition temperature of from 55°C to below 100°C.

[Claim 3]

Toner used for developing an electrostatic latent image as described in claim 1, wherein the fine particle includes an inorganic particle.

[Claim 4]

Toner used for developing an electrostatic latent image as described in claim 1 or 2, wherein the fine particle includes a particulate resin and an inorganic particle.

[Claim 5]

Toner used for developing an electrostatic latent image as described in any one of claims 1, 2 and 4, wherein the particulate resin is crosslinked.

[Claim 6]

Toner for developing an electrostatic latent image as described in any one of claims 1 through 5, wherein an amount of tetrahydrofuran-insoluble binder resin is from 2 to 20 % by

weight.

[Claim 7]

A developer comprising:

a carrier comprising a surface layer formed of at least one of an acrylic resin and a silicone resin; and
the toner for developing the electrostatic latent image as described in any one of claims 1 through 6.

[Claim 8]

A fixing method for fixing an unfixed toner image formed on a recording medium,
the fixing method being characterized in that:
the recording medium passes through a nip portion formed by a heated fixing belt and a pressurizing member, thereby fixing the recording medium with heat and pressure-contact;
the fixing belt winds around the pressurizing member before the nip portion;
the nip has a shape which is concave to the fixing belt side contacting the toner image; and
the toner for developing the electrostatic latent image as described in any one of claims 1 through 6 are used.

[Detailed description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to toner and a developer for developing an electrostatic latent image formed by an image forming method such as electrophotography, electrostatic recording and electrostatic printing, and a method for fixing the toner to a recording medium such as a sheet of paper.

[0002]

[Background Art]

In the case of dry system, the electrostatic latent image formed by electrophotography, electrostatic printing method, electrostatic recording method, and the like, is developed by a dry type toner mainly including binder resins charged by friction by means of a charge applying member, and a colorant, and thereafter, is transferred and fixed on a copy sheet. In this case, in order to obtain a high quality image, one of the most important technical issues is capability of developing the latent image formed on a photoreceptor with toner with higher precision at any occasion of image formation, and thus, the various studies have been continuously performed.

Features requested for the developer in order to achieve a high image quality includes properties related to storage (blocking-resistant property), conveyance, development, transferring, charging and fixing.

[0003]

In general, as a method for fixing a toner image of dry type to a recording medium, a contact-heat fixing method is widely

used, in which a roller or a belt with a smooth surface is heated and a pressure is given with toner. In this method, there are merits that the thermal efficiency is high and a high-speed fixation is possible, and the color toner may be given glossiness and transparency. In contrast, since the surface of the heating and fixing member and the toner in a melting state are contacted with pressure, and separated, part of the toner image may deposit on a surface of the fixing roller to thereby be transferred to another image, i.e., an offset phenomenon may occur. In attempting to avoid the offset problem, methods in which a release oil such as silicone oils is applied to the surface of a fixing roller have been typically used. The methods are useful for preventing occurrence of the offset problem, but it is necessary to provide an applicator applying such a release oil, resulting in jumboization of the fixing device and increase in costs of the fixing device. Therefore, in the case of a monochrome toner, a technique in which the viscoelasticity of the toner is increased, for example, by controlling the molecular weight distribution of the resin included in the toner is used for preventing internal fracture of the toner melted by a heat roller, while adding a release agent such as waxes to the toner to improve the release property of the toner. Thus, fixing methods which use the technique and in which no oil or a small amount of oil is applied to a fixing roller are typically used now.

[0004]

Recently, a strong need exists for energy-saving image forming apparatus such as copiers and printers. Therefore a need exists for toner having a low temperature fixability. In order to improve the low temperature fixability of toner is improved, the viscoelasticity of the toner needs to be decreased when the toner is melted, resulting in occurrence of the offset problem. It is effective to decrease the glass transition temperature (T_g) of the binder resin of toner when improving the low temperature fixability of the toner. In this case, the preservability of the toner deteriorates.

On the other hand, when full color images are formed, yellow, magenta and cyan toner, optionally together with black toner, are typically used. In order to produce full color images having good color reproducibility, the surface of the toner images needs to be smoothed to some extent to decrease light scattering and therefore the viscoelasticity of the toner needs to be decreased when the toner is melted. In this case, the color toner tends to cause the offset problem. In addition, when a release agent is included in the color toner, the adhesion of the toner particles to each other is increased, whereby the transferability of the toner is deteriorated. Therefore, it is difficult to use a fixing method for fixing color images, in which no oil or a small amount of oil is applied to a fixing roller.

[0005]

Under such circumstances, the following types of toner been proposed:

- (1) Toner prepared by covering mother toner particles having a flow starting temperature not higher than 110°C with small particles while embedding the small particles into the mother toner particles (See for example Patent Document No. 1);
- (2) Toner prepared by covering a styrene-acrylic core material having a glass transition temperature of from 50 to 70°C with a styrene based shell material having a higher molecular weight and a higher glass transition temperature (See for example Patent Document No. 2);
- (3) Toner prepared by fixing a particulate resin on mother toner particles using a mechanical impacting method to reform the surface of the mother toner particles (See for example Patent Document No. 3);
- (4) Toner prepared by microencapsulating a core material such as saturated fatty acids and saturated alcohols, which has a melting point of from 40 to 100°C and which is suspended in water, with a particulate resin (See for example Patent Document No. 4);
- (5) Toner prepared by overlaying a thermally stable layer and a thermoplastic resin layer having a Tg not lower than 65°C on the surface of a particulate resin having a low viscosity (See for example Patent Document No. 5);
- (6) Toner prepared by adhering a particulate resin having a Tg of from 60 to 110°C on the surface of toner particles including a resin having a Tg of from 25 to 55°C (See for example Patent Document No. 6);
- (7) Toner including a linear polyester resin having a softening point of from 90 to 120°C and a carnauba wax (See for example Patent Document No. 7);
- (8) Polymerized toner including a wax therein (See for example Patent Document No. 8); and
- (9) Toner prepared by extending or crosslinking an isocyanate-group-containing prepolymer in an aqueous medium using an amine (See for example Patent Document No. 9).

[0006]

However, these toner does not necessarily have a good combination of low temperature fixability, offset resistance, preservability and transferability. Namely, the toner having a shell/core structure in which the shell is a uniform layer have poor low temperature fixability. The toner having a particulate shell has a low viscoelasticity when the toner is melted, whereby the offset resistance is not satisfactory because the toner does not include a release agent. In general, wax tends to be mainly present on the surface of pulverized toner because the kneaded mixture tends to be fractured at interfaces

between the wax and a resin. Therefore the pulverized toner tend to have poor transferability although having good offset resistance. In contrast, polymerized toner in which toner particles are prepared in an aqueous medium have poor offset resistance although having good transferability, because wax tends to be present inside of toner particles.

[0007]

[Patent Document 1]

Japanese Patent No. 2750853 (Claim 1, lines 2 to 10, first column on page 1)

[Patent Document 2]

Japanese Patent Laid-open Publication No. Hei 5-181301 (Abstract, 1st line to the bottom, left lower column on page 1)

[Patent Document 3]

Japanese Patent Laid-open Publication No. Hei 6-342224 (paragraph [0036], the 6th column, page 4)

[Patent Document 4]

Japanese Patent Laid-open Publication No. Hei 8-254853 (Claim 1, lines 2 to 7, 1st column on page 2)

[Patent Document 5]

Japanese Patent Laid-open Publication No. Hei 9-258480 (Claim 1, lines 2 to 7, 1st column on page 2)

[Patent Document 6]

Japanese Patent Laid-open Publication No. 2001-175025 (Claim 1, lines 2 to 7, 1st column on page 2)

[Patent Document 7]

Japanese Patent Laid-open Publication No. Hei 8-220808 (Claim 1, lines 2 to 12, 1st column on page 2)

[Patent Document 8]

Japanese Patent Laid-open Publication No. Hei 5-61242 (paragraphs [0030][0031], 4th column on page 3)

[Patent Document 9]

Japanese Patent Laid-open Publication No. Hei 11-149180 (Claim 1, lines 2 to 8, 1st column, page 2)

[0008]

[Problems to be Solved by the Invention]

An objective of the present invention is to provide color toner and developer having an excellent low temperature fixability compared to the conventional toner or developer, satisfactory offset resistance even if release oil is not applied or a very small amount of release oil is applied to a fixing roller. A further objective of the present invention is to provide a fixing method showing an excellent low temperature fixability and offset resistance using such toner.

[0009]

[Means for Solving the Problems]

After an accumulated study for solving the above problems,

the inventors of the present invention found the toner as a solution for the raised problems through a forming method of a specific toner particle using a specific binder resin and a particulate material.

Specifically, the above problem may be solved by the following inventions related to the toner, developer and fixing method:

(1) Toner, used for developing an electrostatic latent image, obtained in such a manner that:

toner particles including: a binder resin including a modified polyester resin being capable of reacting with active hydrogen, and a low molecular resin with a weight average molecular weight of from 2,000 to 10,000; a colorant; and a release agent; are dissolved or dispersed in an organic solvent, to be made into particles as well as subjected to a polymerization reaction in an aqueous medium, and the solvent is obtained from the solution by methods including removing, cleaning and drying,

wherein the binder resin has a glass transition temperature of from 35°C to below 55 °C, and fine particles with an average diameter of from 0.002 to 0.2 times that of the toner particles are embedded in the surface of toner.

(2) Toner used for developing an electrostatic latent image as described in (1), wherein the fine particle includes a particulate resin having a glass transition temperature of from 55°C to below 100°C.

(3) Toner used for developing an electrostatic latent image as described in (1), wherein the fine particle includes an inorganic particle.

(4) Toner used for developing an electrostatic latent image as described in (1) or (2), wherein the fine particle includes a particulate resin and an inorganic particle.

(5) Toner used for developing an electrostatic latent image as described in any one of (1), (2) and (4), wherein the particulate resin is crosslinked.

(6) Toner used for developing an electrostatic latent image as described in any one of (1) through (5), wherein an amount of tetrahydrofuran-insoluble binder resin is from 2 to 20 % by weight.

(7) A developer including:
a carrier including a surface layer formed of at least one of an acrylic resin and a silicone resin; and
the toner for developing the electrostatic latent image as described in any one of (1) through (6).

(8) A fixing method for fixing an unfixed toner image formed on a recording medium,
the fixing method being characterized in that:
the recording medium passes through a nip portion formed

by a heated fixing belt and a pressurizing member, thereby fixing the recording medium with heat and pressure-contact;

the fixing belt winds around the pressurizing member before the nip portion;

the nip has a shape which is concave to the fixing belt side contacting the toner image; and

the toner for developing the electrostatic latent image as described in any one of (1) through (6) are used.

[0010]

[Embodiments of the Invention]

The present invention relates to an improved toner for image formation formed of a mixture at least including a binder resin, a colorant and a releasing agent and is characterized as follows:

(1) The toner of the present invention can be prepared by dissolving a composition including at least a modified polyester resin in an organic solvent to prepare an oil phase liquid; dispersing the oil phase liquid in an aqueous medium including a particulate material such as particulate resins and/or inorganic particulate materials while subjecting the polyester resin to a reaction such as addition polymerization using a crosslinking agent and/or an extending agent to prepare particles; removing the solvents to obtain toner particles; and washing the toner particles to prepare dry toner particles.

(2) The binder resin in the toner of the present invention has a glass transition temperature lower than those of binder resins for use in normal toner, and the particulate material are present on the surface of the toner particles (while embedded into the surface).

The typical state of the particulate material present on the surface of the toner of the present invention is as illustrated in Figs. 1(a) and 1(b), and the particulate material is present on the surface portion of the toner particles while substantially separated from each other without causing agglomeration. In addition, the particulate material is substantially separated from each other in the depth direction of the toner particles. Namely the particulate material is substantially separated from the other toner constituents such as binder resins therebetween.

[0011]

Materials and the production method to be used in the present invention will now be described in detail.

(Binder resin)

The binder resin used in the toner of the present invention includes urea-modified polyester resins highly polymerized with a urea bonding and a known binding resin for toner with a relatively low molecular weight as essential components. A feature of a urea-modified polyester resin (i) is a good offset resistance, and examples thereof includes reaction products of a polyester

prepolymer (A) with an amine (B).

[0012]

Polyesterprepolymers (A) having an isocyanate group include, for example, compounds prepared by reacting a polycondensation product of a polyol (1) and a polycarboxylic acid (2), which has a group having an active hydrogen, with a polyisocyanate (3) are used.

[0013]

Suitable groups having an active hydrogen include a hydroxyl group (an alcoholichydroxyl group and a phenolichydroxyl group), an amino group, a carboxyl group, a mercapto group, etc. Among these groups, alcoholic hydroxyl groups are preferable.

[0014]

Suitable polyols (1) include diols (1-1) and polyols (1-2) having three or more hydroxyl groups. Preferably diols (1-1) or mixtures in which a small amount of a polyol (1-2) is added to a diol (1-1) are used. Specific examples of the diols (1-1) include alkylene glycol (e.g., ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol and 1,6-hexanediol); alkylene ether glycols (e.g., diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol and polytetramethylene ether glycol); alicyclic diols (e.g., 1,4-cyclohexane dimethanol and hydrogenated bisphenol A); bisphenols (e.g., bisphenol A, bisphenol F and bisphenol S); adducts of the alicyclic diols mentioned above with an alkylene oxide (e.g., ethylene oxide, propylene oxide and butylene oxide); adducts of the bisphenols mentioned above with an alkylene oxide (e.g., ethylene oxide, propylene oxide and butylene oxide); etc. Among these compounds, alkylene glycols having from 2 to 12 carbon atoms and adducts of bisphenols with an alkylene oxide are preferable. More preferably, adducts of bisphenols with an alkylene oxide, or mixtures of an adduct of bisphenols with an alkylene oxide and an alkylene glycol having from 2 to 12 carbon atoms are used. Specific examples of the polyols (1-2) include aliphatic alcohols having three or more hydroxyl groups (e.g., glycerin, trimethylol ethane, trimethylol propane, pentaerythritol and sorbitol); polyphenols having three or more hydroxyl groups (trisphenol PA, phenol novolak and cresol novolak); adducts of the polyphenols mentioned above with an alkylene oxide; etc.

[0015]

Suitable polycarboxylic acids (2) include dicarboxylic acids (2-1) and polycarboxylic acids (2-2) having three or more carboxyl groups. Preferably dicarboxylic acids (2-1) or mixtures in which a small amount of a polycarboxylic acid (2-2) is added to a dicarboxylic acid (2-1) are used.

Specific examples of the dicarboxylic acids (2-1) include alkylene dicarboxylic acids (e.g., succinic acid, adipic acid

and sebacic acid); alkenylene dicarboxylic acids (e.g., maleic acid and fumaric acid); aromatic dicarboxylic acids (e.g., phthalic acid, isophthalic acid, terephthalic acid and naphthalene dicarboxylic acids); etc. Among these compounds, alkenylene dicarboxylic acids having from 4 to 20 carbon atoms and aromatic dicarboxylic acids having from 8 to 20 carbon atoms are preferably used. Specific examples of the polycarboxylic acids (2-2) having three or more hydroxyl groups include aromatic polycarboxylic acids having from 9 to 20 carbon atoms (e.g., trimellitic acid and pyromellitic acid). As the polycarboxylic acid (2), anhydrides or lower alkyl esters (e.g., methyl esters, ethyl esters or isopropyl esters) of the polycarboxylic acids mentioned above can be used for the reaction with a polyol (1). Suitable mixing ratio (i.e., an equivalence ratio $[OH]/[COOH]$) of a polyol (1) to a polycarboxylic acid (2) is from 2/1 to 1/1, preferably from 1.5/1 to 1/1 and more preferably from 1.3/1 to 1.02/1.

[0016]

Specific examples of the polyisocyanates (3) include aliphatic polyisocyanates (e.g., tetramethylene diisocyanate, hexamethylene diisocyanate and 2,6-diisocyanate methylcaproate); alicyclic polyisocyanates (e.g., isophorone diisocyanate and cyclohexylmethane diisocyanate); aromatic didicosyantes (e.g., tolylene diisocyanate and diphenylmethane diisocyanate); aromatic aliphatic diisocyanates (e.g., α , α , α , α -tetramethylxylene diisocyanate); isocyanurates; blocked polyisocyanates in which the polyisocyanates mentioned above are blocked with phenol derivatives, oximes or caprolactams; etc. These compounds can be used alone or in combination.

[0017]

Suitable mixing ratio of a polyisocyanate (3), as a ratio $[NCO]/[OH]$ of isocyanate group $[NCO]$ against hydroxyl group $[OH]$ of the polyester having a hydroxyl group, is from 5/1 to 1/1, preferably from 4/1 to 1.2/1 and more preferably from 2.5/1 to 1.5/1. When the $[NCO]/[OH]$ ratio is over 5, the low temperature fixability of the toner deteriorates. In contrast, when the molar ratio $[NCO]$ is less than 1, the content of the urea group in the modified polyesters decreases, whereby the hot-offset resistance of the toner deteriorates. The content of the constitutional component of a polyisocyanate (3) in the polyester prepolymer (A) having a polyisocyanate group at its end portion is from 0.5 to 40 % by weight, preferably from 1 to 30 % by weight and more preferably from 2 to 20 % by weight. When the content is less than 0.5 % by weight, the hot offset resistance of the toner deteriorates and in addition the heat resistance and low temperature fixability of the toner also deteriorate. In contrast, when the content exceeds 40 % by weight, the low temperature fixability of the toner deteriorates.

[0018]

The number of the isocyanate group included in a molecule of the polyester prepolymer (A) is not less than 1, preferably from 1.5 to 3, and more preferably from 1.8 to 2.5. When the number of the isocyanate group is below 1, the molecular weight of the resultant urea-modified polyester decreases, whereby the hot offset resistance deteriorate.

[0019]

Specific examples of the amines (B) include diamines (B1), polyamines (B2) having three or more amino groups, amino alcohols (B3), amino mercaptans (B4), amino acids (B5) and blocked amines (B6) in which the amines (B1-B5) mentioned above are blocked.

Specific examples of the amines (1) include aromatic diamines (e.g., phenylene diamine, diethyltoluene diamine and 4,4'-diaminodiphenyl methane); alicyclic diamines (e.g., 4,4'-diamino-3,3'-dimethyldicyclohexyl methane, diaminocyclohexane and isophoron diamine); aliphatic diamines (e.g., ethylene diamine, tetramethylene diamine and hexamethylene diamine); etc. Specific examples of the polyamines (B2) having three or more amino groups include diethylene triamine, triethylene tetramine. Specific examples of the amino alcohols (B3) include ethanol amine and hydroxyethyl aniline. Specific examples of the aminomercaptan (B4) include aminoethyl mercaptan and aminopropyl mercaptan. Specific examples of the amino acids (B5) include amino propionic acid and amino caproic acid. Specific examples of the blocked amines (B6) include ketimine compounds which are prepared by reacting one of the amines B1-B5 mentioned above with a ketone such as acetone, methyl ethyl ketone and methyl isobutyl ketone; oxazoline compounds, etc. Among these compounds, diamines (B1) and mixtures in which a diamine is mixed with a small amount of a polyamine (B2).

The molecular weight of the urea-modified polyesters can be controlled using an elongation ant catalyst, if desired. Specific examples of the elongation anticatalyst include monoamines (e.g., diethyle amine, dibutyl amine, butyl amine and lauryl amine), and blocked amines (i.e., ketimine compounds) prepared by blocking the monoamines mentioned above.

[0020]

The mixing ratio (i.e., a ratio $[NCO] / [NHx]$) of the content of the prepolymer (A) having an isocyanate group to the amine (B) is from 1/2 to 2/1, preferably from 1.5/1 to 1/1.5 and more preferably from 1.2/1 to 1/1.2. When the mixing ratio is over 2, or below 1/2, the molecular weight of the resultant urea-modified polyester decreases, resulting in deterioration of the hot offset resistance of the resultant toner.

The urea-modified polyesters may include a urethane bonding as well as a urea bonding. The molar ratio (urea/urethane) of the urea bonding to the urethane bonding is from 100/0 to 10/90,

preferably from 80/20 to 20/80 and more preferably from 60/40 to 30/70. When the mol ratio of the urea bonding is below 10%, the hot offset resistance of the resultant toner deteriorates.

The urea-modified polyesters (i) can be prepared, for example, by a method such as one-shot methods or prepolymer methods. The weight average molecular weight of the urea-modified polyesters is not less than 10,000, preferably from 15,000 to 10,000,000 and more preferably from 20,000 to 1,000,000. When the weight average molecular weight is below 10,000, the hot offset resistance of the resultant toner deteriorates.

[0021]

The binder resin having a relatively low molecular weight has an advantage of low temperature fixation. Specific examples thereof include styrene polymers and substituted styrene polymers such as polystyrene, poly-p-chlorostyrene and polyvinyltoluene; styrene copolymers such as styrene-p-chlorostyrene copolymers, styrene-propylene copolymers, styrene-vinyltoluene copolymers, styrene-vinylnaphthalene copolymers, styrene-methyl acrylate copolymers, styrene-ethyl acrylate copolymers, styrene-butyl acrylate copolymers, styrene-octyl acrylate copolymers, styrene-methyl methacrylate copolymers, styrene-ethyl methacrylate copolymers, styrene-butyl methacrylate copolymers, styrene-methyl α -chloromethacrylate copolymers, styrene-acrylonitrile copolymers, styrene-vinyl methyl ketone copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, styrene-acrylonitrile-indene copolymers, styrene-maleic acid copolymers and styrene-maleic acid ester copolymers; and other resins such as polymethyl methacrylate, polybutyl methacrylate, polyvinyl chloride, polyvinyl acetate, polyethylene, polypropylene, polyesters, epoxy resins, epoxy polyol resins, polyurethane resins, polyamide resins, polyvinyl butyral resins, acrylic resins, rosin, modified rosins, terpene resins, aliphatic or alicyclic hydrocarbon resins, aromatic petroleum resins, chlorinated paraffin, paraffin waxes, etc. These resins are used alone or in combination.

The low molecular polyester preferably has a weight average molecular weight of from 2,000 to 10,000 and a glass transition temperature (T_g) of not less than 35°C and less than 55°C.

Among these resins, polyester resins, epoxy resins, and epoxy polyol resins are preferably used.

Suitable unmodified polyester resins include polycondensation products of a polyol (1) with a polycarboxylic acid (2). In addition, as the unmodified polyester resins, polyester resins modified by a bonding (such as urethane bonding) other than a urea bonding, can also be used as well as the unmodified polyester resins mentioned above.

[0022]

The mixing ratio of the urea modified polyester resin (i) and the toner binding resin of a relatively low molecular weight (ii) is normally from 5/95 to 60/40, preferably from 5/95 to 30/70. When the amount of (i) is less than 5% by weight, the hot offset resistance becomes insufficient, and when more than 60% by weight, low temperature fixability deteriorates.

In addition, resins other than the urea-modified polyester resins (i) and the toner binder resin with a relatively low molecular weight (ii) can be included in the toner in an amount (normally less than 30% by weight) such that the fixing properties of the resultant toner are not deteriorated.

However, due to the low temperature fixation, when Tg of the toner is measured, Tg value for the binder resin needs to be in a range from 35°C and lower than 55°C. When the Tg of the toner is more than 56°C, the resultant toner has poor low temperature fixability. In contrast, when the Tg is less than 35°C, the resultant toner has poor preservability and blocking problem occurs in the machine.

[0023]

The binder resin included in the toner of the present invention preferably includes THF(tetrahydrofuran)-insoluble moieties (or THF-insoluble components) therein to impart good offset resistance to the toner. Such THF(tetrahydrofuran)-insoluble moieties can be incorporated in a resin by a known method using a monomer having three or more functional groups when synthesizing the resin. Specifically, urea-modified polyester resins prepared by using a prepolymer having an isocyanate group in an amount of from 1.5 to 3.0 pieces in average, and preferably from 2.1 to 2.8 pieces in average, in a molecule of the prepolymer are preferably used as the urea-modified polyester resin.

The percentage of THF-insoluble components in the binder resin of the toner of the present invention is preferably from 1 to 30% by weight, and more preferably from 2 to 30 % by weight, based on the total weight of the binder resin to impart a good combination of hot offset resistance and low temperature fixability to the resultant toner. Namely, when the percentage of THF-insoluble components is below 2%, the resultant toner has poor hot offset resistance. In contrast, when the percentage is over 30%, the toner has poor low temperature fixability.

[0024]

The percentage of THF-insoluble components in the binder resin included in toner is determined as follows:

- (1) toner sample of about 1.0 gram is precisely weighed;
- (2) the toner is mixed with 50 grams of THF and is allowed to settle at 20°C for 24 hours;
- (3) the mixture is filtered using a filter paper 5C

specified in JIS (Japanese Industrial Standards) P3801 whose weight is preliminarily measured;

(4) the filter paper is dried to remove THF therefrom; and

(5) the filter paper is weighed to determine the weight of the THF insoluble materials.

At this point, the weight of the THF-insoluble solids included in the toner, such as colorants and waxes, should be subtracted from the weight of the THF insoluble materials, which is determined by another method such as thermometric analysis, to determine the THF-insoluble components in the binder resin in the toner.

[0025]

The molecular weight distribution of the components in the toner, which are soluble in tetrahydrofuran, is measured as follows:

(1) toner of about 1 gram is precisely weighed;

(2) the toner is mixed with tetrahydrofuran to prepare a tetrahydrofuran solution of the THF-soluble components at a concentration of from 0.05 to 0.6 % by weight;

(3) the sample solution is filtered using a filter for liquid chromatography to remove THF-insoluble components therefrom;

(4) tetrahydrofuran is flown through a column, which is heated to 40 °C in a heat chamber, at a flow rate of 1 ml/min and 200 μ l of the sample solution is injected thereto to determine the molecular weight distribution of the binder resin using a working curve which shows the relationship between a molecular weight and counts detected by GPC (gel permeation chromatography) and which is previously prepared using at least ten polystyrenes having a single molecular distribution such as 6×10^2 , 2.1×10^3 , 4×10^3 , 1.75×10^4 , 5.1×10^4 , 1.1×10^5 , 3.9×10^5 , 8.6×10^5 , 2×10^6 , and 4.48×10^6 , which are prepared by Pressure Chemical Co., or Toyoh Soda Corporation. 10 pieces of standard polystyrene samples may preferably be used. In addition, as the detector, a refractive index (RI) detector is used.

Tg of the binder resin is measured by Rigaku THRMOFLEX TG8110 manufactured by Rigaku Electric Corporation under the conditions of temperature rising speed of 10°C/min, and the shoulder value in the 2nd run is taken as the Tg value.

[0026]

The toner of the present invention includes a release agent. Known release agents for use in conventional toner can be used in the toner of the present invention. Suitable release agents include polyolefin waxes (e.g., polyethylene waxes and polypropylene waxes); hydrocarbons having a long chain (e.g., paraffin waxes and SASOL waxes); and waxes having a carbonyl

group. Among these materials, waxes having a carbonyl group are preferably used for the toner of the present invention.

Specific examples of the waxes including a carbonyl group include polyalkanoic acid esters such as carnauba wax, montan waxes, trimethylolpropane tribehenate, pentaerythritol tetrabehehenate, pentaerythritol diacetate dibehenate, glycerin tribehenate, and 1,18-octadecanediol distearate; polyalkanol esters such as tristearyl trimellitate, and distearyl maleate; polyalkanoic acid amides such as ethylenediamine dibehenylamide; polyalkylamide such as trimellitic acid tristearylamide; dialkyl ketone such as distearyl ketone; etc. Among these materials, polyalkanoic acid esters are preferable.

The release agent for use in the toner of the present invention preferably has a melting point of from 60 to 120 °C, to impart good low temperature fixability to the toner.

The content of the release agent in the toner is preferably from 3 to 30 % by weight based on total weight of the toner. In this case, the resultant toner has a good releasing property without causing a spent-carrier problem, toner filming problem, a developing ability decreasing problem and a transferability decreasing problem.

[0027]

(Particulate resin)

As the particulate resin for use in the toner of the present invention, known particulate resins can be used if the resins can be dispersed in an aqueous liquid. Specific examples of the particulate resins include particles of vinyl resins, polyurethane resins, epoxy resins, polyester resins, polyamide resins, polyimide resins, silicone resins, phenolic resins, melamine resins, urea resins, aniline resins, ionomer resins, polycarbonate resins, etc.

As the particulate resins, these above resins can be used alone or in combination. Among these resins, vinyl resins, polyurethane resins, epoxy resins and polyester resins can be preferably used because aqueous dispersions in which fine spherical resin particles are dispersed in an aqueous liquid can be easily obtained.

Suitable vinyl resins include homopolymers and copolymers of one or more vinyl monomers. Specific examples thereof include styrene-(meth)acrylate copolymers, styrene-butadiene copolymers, (meth)acrylic acid-acrylate copolymers, styrene-acrylonitrile copolymers, styrene-maleic anhydride copolymers, styrene-(meth)acrylic acid copolymers, etc.

[0028]

The average particle diameter of the particulate resin for use in the toner of the present invention is from 0.002 to 0.2 times the average particle diameter of the toner. When the particle diameter is less than 0.002 times, the resultant toner

has poor preservability. In contrast, the particle diameter is more than 0.2 times, the resultant toner has poor low temperature fixability.

The surface of the toner particles is preferably covered by the particulate resin at a cover rate of from 40 to 80 % while the particulate resin is embedded into the toner surface.

When the surface of the toner particles is covered by a continuous layer (i.e., a shell), the toner has poor fixing property. However, when the surface is covered by a discontinuous layer (i.e., a particulate resin), the toner has good fixability and good preservability. This is because the binder resin of the toner easily adheres to a receiving material during fixing (resulting in improvement of good fixability), while contact areas of toner particles decrease (resulting in improvement of preservability).

The particulate resin for use in the toner of the present invention preferably has a Tg of from 55 to 100°C. When the Tg is below 55°C, the resultant toner has poor preservability, and when the Tg is more than 100°C, the resultant toner has poor low temperature fixability.

In addition, when the particulate resin is crosslinked, the toner has good mechanical strength. In this case, the particulate resin has good resistance to organic solvents used for preparing toner particles, and thus, the particulate resin is present on the surface of the toner particles while maintaining its form.

[0029]

(Inorganic particulate material)

As the inorganic particulate material for use in the toner of the present invention, known inorganic particulate materials can be used if the materials can be dispersed in an aqueous liquid.

Specific examples of such inorganic particulate materials include silica, alumina, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, quartz sand, clay, mica, sand-lime, diatom earth, chromium oxide, cerium oxide, red iron oxide, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium carbonate, silicon carbide, silicon nitride, etc. Among these materials, silica and titanium oxide are preferably used when the toner is used as a negatively charged toner, and alumina and titanium oxide are preferably used when the toner is used as a positively charged toner.

The average particle diameter of the inorganic particulate materials for use in the toner of the present invention is from 0.002 to 0.2 times the average particle diameter of the toner. When the particle diameter is less than 0.002 times, the resultant toner has poor preservability. In contrast, the particle diameter is over than 0.2 times, the resultant toner has poor

low temperature fixability.

The surface of the toner particle is preferably covered with the inorganic particulate material at a cover rate of from 40 to 80 % while the inorganic particulate material is embedded into the toner surface.

These particulate materials (i.e., the particulate resins and inorganic particulate materials) can be used alone or in combination.

The particulate material is included in an aqueous medium to prepare an aqueous phase liquid. A composition including at least a binder resin, a colorant and a release agent is dissolved or dispersed in an organic solvent to prepare an oil phase liquid. Then the oil phase liquid is dispersed in the aqueous phase liquid to adhere the particulate material in the aqueous phase to the particles of the composition, i.e., particles of the oil phase liquid. In this case, by agitating this emulsion, the particulate material is properly embedded into the surface of the composition.

[0030]

(Colorant)

Suitable colorants for use in the toner of the present invention include known dyes and pigments. Specific examples of the colorants include carbon black, Nigrosine dyes, black iron oxide, Naphthol Yellow S, Hansa Yellow (10G, 5G and G), Cadmium Yellow, yellow iron oxide, loess, chrome yellow, Titan Yellow, polyazo yellow, Oil Yellow, Hansa Yellow (GR, A, RN and R), Pigment Yellow L, Benzidine Yellow (G and GR), Permanent Yellow (NCG), Vulcan Fast Yellow (5G and R), Tartrazine Lake, Quinoline Yellow Lake, Anthrazane Yellow BGL, isoindolinone yellow, red iron oxide, red lead, orange lead, cadmium red, cadmium mercury red, antimony orange, Permanent Red 4R, Para Red, Fire Red, p-chloro-o-nitroaniline red, Lithol Fast Scarlet G, Brilliant Fast Scarlet, Brilliant Carmine BS, Permanent Red (F2R, F4R, FRL, FRLl and F4RH), Fast Scarlet VD, Vulcan Fast Rubine B, Brilliant Scarlet G, Lithol Rubine GX, Permanent Red F5R, Brilliant Carmine 6B, Pigment Scarlet 3B, Bordeaux 5B, Toluidine Maroon, Permanent Bordeaux F2K, Helio Bordeaux BL, Bordeaux 10B, BON Maroon Light, BON Maroon Medium, Eosin Lake, Rhodamine Lake B, Rhodamine Lake Y, Alizarine Lake, Thioindigo Red B, Thioindigo Maroon, Oil Red, Quinacridone Red, Pyrazolone Red, polyazo red, Chrome Vermilion, Benzidine Orange, perynone orange, Oil Orange, cobalt blue, cerulean blue, Alkali Blue Lake, Peacock Blue Lake, Victoria Blue Lake, metal-free Phthalocyanine Blue, Phthalocyanine Blue, Fast Sky Blue, Indanthrene Blue (RS and BC), Indigo, ultramarine, Prussian blue, Anthraquinone Blue, Fast Violet B, Methyl Violet Lake, cobalt violet, manganese violet, dioxane violet, Anthraquinone Violet, Chrome Green, zinc green, chromium oxide, viridian, emerald green, Pigment Green B,

Naphthol Green B, Green Gold, Acid Green Lake, Malachite Green Lake, Phthalocyanine Green, Anthraquinone Green, titanium oxide, zinc oxide, lithopone and the like. These materials are used alone or in combination. The content of the colorant in the toner is preferably from 1 to 15 % by weight, and more preferably from 3 to 10 % by weight of the toner.

[0031]

Master batches, which are complexes of the colorants as mentioned above with resins, can be used as the colorant of the toner of the present invention. Specific examples of the resins for use as the binder resin of the master batches include the modified and unmodified polyester resins as mentioned above, styrene polymers and substituted styrene polymers such as polystyrene, poly-p-chlorostyrene and polyvinyltoluene; styrene copolymers such as styrene-p-chlorostyrene copolymers, styrene-propylene copolymers, styrene-vinyltoluene copolymers, styrene-vinylnaphthalene copolymers, styrene-methyl acrylate copolymers, styrene-ethyl acrylate copolymers, styrene-butyl acrylate copolymers, styrene-octyl acrylate copolymers, styrene-methyl methacrylate copolymers, styrene-ethyl methacrylate copolymers, styrene-butyl methacrylate copolymers, styrene-methyl α -chloromethacrylate copolymers, styrene-acrylonitrile copolymers, styrene-vinyl methyl ketone copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, styrene-acrylonitrile-indene copolymers, styrene-maleic acid copolymers and styrene-maleic acid ester copolymers; and other resins such as polymethyl methacrylate, polybutyl methacrylate, polyvinyl chloride, polyvinyl acetate, polyethylene, polypropylene, polyesters, epoxy resins, epoxy polyol resins, polyurethane resins, polyamide resins, polyvinyl butyral resins, acrylic resins, rosin, modified rosins, terpene resins, aliphatic or alicyclic hydrocarbon resins, aromatic petroleum resins, chlorinated paraffin, paraffin waxes, etc. These resins are used alone or in combination.

[0032]

The master batches can be prepared by mixing one or more of the resins as mentioned above and one or more of the colorants as mentioned above and kneading the mixture while applying a high shearing force thereto. In this case, an organic solvent can be added to increase the interaction between the colorant and the resin. In addition, a flashing method in which an aqueous paste including a colorant and water is mixed with a resin dissolved in an organic solvent and kneaded so that the colorant is transferred to the resin side (i.e., the oil phase), and then the organic solvent (and water, if desired) is removed can be preferably used because the resultant wet cake can be used as it is without being dried. When performing the mixing and kneading process, dispersing devices capable of applying a high

shearing force such as three roll mills can be preferably used.

[0033]

(Charge controlling agent)

The toner of the present invention optionally includes a charge controlling agent. Known charge controlling agents can be used for the toner of the present invention. However, when the toner is color toner other than black toner, colorless, white colored or pale colored charge controlling agents are preferably used. Specific examples of the charge controlling agent include triphenyl methane dyes, chelate compounds of molybdcic acid, Rhodamine dyes, alkoxyamines, quaternary ammonium salts (including fluorine-modified quaternary ammonium salts), alkylamides, phosphor and compounds including phosphor, tungsten and compounds including tungsten, fluorine-containing activators, metal salts of salicylic acid, metal salts of salicylic acid derivatives, etc. Specific examples of the marketed products of the charge controlling agents include BONTRON P-51 (quaternary ammonium salt), BONTRON E-82 (metal complex of oxynaphthoic acid), BONTRON E-84 (metal complex of salicylic acid), and BONTRON E-89 (phenolic condensation product), which are manufactured by Orient Chemical Industries Co., Ltd.; TP-302 and TP-415 (molybdenum complex of quaternary ammonium salt), which are manufactured by Hodogaya Chemical Co., Ltd.; COPY CHARGE PSY VP2038 (quaternary ammonium salt), COPY BLUE (triphenyl methane derivative), COPY CHARGE NEG VP2036 and COPY CHARGE NX VP434 (quaternary ammonium salt), which are manufactured by Hoechst AG; LRA-901, and LR-147 (boron complex), which are manufactured by Japan Carlit Co., Ltd.; quinacridone, azo pigments, and polymers having a functional group such as a sulfonate group, a carboxyl group, a quaternary ammonium group, etc.

It is preferable that the charge controlling agent is included in the toner in an amount of from 0.1 to 5 parts by weight per 100 parts by weight of the binder resin. The charge controlling agent can be preliminarily mixed and kneaded with master batches and resins or can be added to an organic solvent while being dissolved or dispersed directly in the organic solvent. Alternatively, the charge controlling agent may be mixed with toner particles prepared so as to be fixed on the surface thereof.

[0034]

(External additive)

The toner of the present invention preferably includes an external additive. Inorganic fine particles are typically used as an external additive. Inorganic particulate materials having a primary particle diameter of from 5 μ m to 2 μ m, and preferably from 5 μ m to 500 μ m are used. The surface area of the inorganic particulate materials is preferably from 20 to 500 m^2/g when measured by a BET method. The content of the inorganic

particulate material in the toner is preferably from 0.01 % to 5.0 % by weight, and more preferably from 0.01 % to 2.0 % by weight, based on the total weight of the toner. Specific examples of such inorganic particulate materials include silica, alumina, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, quartz sand, clay, mica, sand-lime, diatom earth, chromium oxide, cerium oxide, red iron oxide, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium carbonate, silicon carbide, silicon nitride, etc.

[0035]

Suitable hydrophobizing agents for use in the hydrophobizing treatment include silane coupling agents, silylation agents, silane coupling agents having a fluorinated alkyl group, organic titanate coupling agents, aluminum coupling agents, silicone oils, modified silicone oils, etc.

Specific examples for cleanability improving agent for removing the developer after transfer remaining on the photoreceptor or the primary transfer medium include fatty acids and their metal salts such as stearic acid, zinc stearate, and calcium stearate; and particulate polymers such as polymethyl methacrylate and polystyrene, which are manufactured by a method such as soap-free emulsion polymerization methods.

[0036]

The toner of the present invention is prepared, for example, by the following method, but the manufacturing method is not limited thereto.

(Toner manufacturing method in an aqueous medium)

Suitable aqueous media for use in the toner manufacturing method of the present invention include water and mixtures of water and a solvent which can be mixed with water. Specific examples of such a solvent include alcohols (e.g., methanol, isopropanol and ethylene glycol), dimethylformamide, tetrahydrofuran, cellosolves (e.g., methyl cellosolve), lower ketones (e.g., acetone and methyl ethyl ketone), etc.

An emulsifier and a particulate material as mentioned above (i.e., a particulate resin and/or an inorganic particulate material) are dissolved/dispersed in an aqueous medium to prepare an aqueous phase liquid.

Toner particles can be prepared as follows:

- (1) a composition including a prepolymer (A) having an isocyanate group, a low molecular polyester having a relatively low molecular weight, a colorant, a release agent, a charge controlling agent and the like is dissolved/dispersed in an organic solvent to prepare a dispersion (i.e., an oil phase liquid);
- (2) the dispersion is mixed with an amine (B);
- (3) the mixture is dispersed in the aqueous phase liquid while

a shearing force is applied thereto to prepare an emulsion having a desired particle diameter;

(4) the emulsion is optionally heated to perform a urea reaction of the prepolymer (A) with the amine (B);

(5) the solvents are removed from the reaction product to obtain particles; and

(6) the particles are washed and dried, resulting in formation of toner particles in which the particulate material is adhered to the surface of the toner particles while embedded therein.

Before the composition is dissolved/dispersed in an organic solvent, toner constituents such as the colorant, release agent and charge controlling agent are preferably mixed such that the components are finely dispersed in the mixture. In addition, after forming the particulate not including the colorant, the colorant may be added with a publicly known dyeing method.

[0037]

The representative toner manufacturing methods have been described briefly, and a further detailed explanation will now be given.

The method for preparing the emulsion is not particularly limited, and low speed shearing methods, high speed shearing methods, friction methods, high pressure jet methods, ultrasonic methods, etc. can be used. Among these methods, high speed shearing methods are preferable because particles having a particle diameter of from 2 μm to 20 μm can be easily prepared. When a high speed shearing type dispersion machine is used, the rotation speed is not particularly limited, but the rotation speed is typically from 1,000 to 30,000 rpm, and preferably from 5,000 to 20,000 rpm. The dispersion time is not also particularly limited, but is typically from 0.5 to 15 minutes for a batch production method. The temperature in the dispersion process is typically from 0 to 150 °C (under pressure), and more preferably from 20 to 80 °C. . When the emulsion is prepared, the weight ratio (T/M) of the composition (T) (including a prepolymer (A)) to the aqueous medium (M) is typically from 100/50 to 100/2,000, and preferably from 100/100 to 100/1,000. When the quantity of the aqueous medium is less than 50 parts, the dispersion of the toner constituents in the aqueous medium is not satisfactory, whereby the resultant toner particles do not have a desired particle diameter. In contrast, the quantity of the aqueous medium is over 20,000. When the emulsion is prepared, a dispersant can be preferably used so that the emulsion includes particles having a sharp particle diameter distribution and the emulsion has good dispersion stability. Specific examples of the dispersants which are used for emulsifying an oil phase liquid, in which toner constituents are dissolved or dispersed, in an aqueous phase liquid, include anionic surfactants such as alkylbenzene sulfonic acid salts, α -olefin sulfonic acid salts,

and phosphoric acid salts; cationic surfactants such as amine salts (e.g., alkyl amine salts, aminoalcohol fatty acid derivatives, polyamine fatty acid derivatives and imidazoline), and quaternary ammonium salts (e.g., alkyltrimethyl ammonium salts, dialkyldimethyl ammonium salts, alkyldimethyl benzyl ammonium salts, pyridinium salts, alkyl isoquinolinium salts and benzethonium chloride); nonionic surfactants such as fatty acid amide derivatives, polyhydric alcohol derivatives; and ampholytic surfactants such as alanine, dodecyl di(aminoethyl)glycin, di(octylaminoethyl)glycin, and N-alkyl-N,N-dimethylammonium betaine.

[0038]

By using a surfactant having a fluoroalkyl group, a dispersion having good dispersibility can be prepared even when the amount of the surfactant is small. Specific examples of anionic surfactants having a fluoroalkyl group include fluoroalkyl carboxylic acids having from 2 to 10 carbon atoms and their metal salts, disodium perfluorooctanesulfonylglutamate, sodium 3-{omega-fluoroalkyl(C6-C11)oxy}-1-alkyl(C3-C4).sulfonate, sodium 3-{omega-fluoroalkanoyl(C6-C8)-N-ethylamino}-1-propanesulfonate, fluoroalkyl(C11-C20) carboxylic acids and their metal salts, perfluoroalkylcarboxylic acids and their metal salts, perfluoroalkyl(C4-C12)sulfonate and their metal salts, perfluorooctanesulfonic acid diethanol amides, N-propyl-N-(2-hydroxyethyl)perfluorooctanesulfonamide, perfluoroalkyl(C6-C10)sulfonamidepropyltrimethylammonium salts, salts of perfluoroalkyl(C6-C10)-N-ethylsulfonyl glycin, monoperfluoroalkyl(C6-C16)ethylphosphates, etc.

[0039]

Specific examples of the marketed products of such surfactants include SURFLON S-111, S-112 and S-113, which are manufactured by Asahi Glass Co., Ltd.; FRORARD FC-93, FC-95, FC-98 and FC-129, which are manufactured by Sumitomo 3M Ltd.; UNIDYNE DS-101 and DS-102, which are manufactured by Daikin Industries, Ltd.; MEGAFACE F-110, F-120, F-113, F-191, F-812 and F-833 which are manufactured by Dainippon Ink and Chemicals, Inc.; ECTOP EF-102, 103, 104, 105, 112, 123A, 306A, 501, 201 and 204, which are manufactured by Tohchem Products Co., Ltd.; FUTARGENT F-100 and F150 manufactured by Neos; etc.

[0040]

Specific examples of the cationic surfactants, which can disperse an oil phase liquid including toner constituents in water, include primary, secondary and tertiary aliphatic amines having a fluoroalkyl group, aliphatic quaternary ammonium salts such as perfluoroalkyl(C6-C10)sulfonamidepropyltrimethylammonium

salts, benzalkonium salts, benzetonium chloride, pyridinium salts, imidazolinium salts, etc. Specific examples of the marketed products thereof include SURFLONS-121 (from Asahi Glass Co., Ltd.); FRORARD FC-135 (from Sumitomo 3M Ltd.); UNIDYNES-202 (from Daikin Industries, Ltd.); MEGAFACE F-150 and F-824 (from Dainippon Ink and Chemicals, Inc.); ECTOP EF-132 (from Tochem Products Co., Ltd.); FUTARGENT F-300 (from Neos); etc.

In addition, inorganic dispersants, which are hardly soluble in water, such as tricalcium phosphate, calcium carbonate, titanium oxide, colloidal silica, and hydroxyapatite can also be used.

[0041]

Further, it is possible to stably disperse (emulsify) toner constituents in water using a polymeric protection colloid. Specific examples of such protection colloids include polymers and copolymers prepared using monomers such as acids (e.g., acrylic acid, methacrylic acid, α -cyanoacrylic acid, α -cyanomethacrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic acid and maleic anhydride), acrylic monomers having a hydroxyl group (e.g., β -hydroxyethyl acrylate, β -hydroxyethyl methacrylate, β -hydroxypropyl acrylate, β -hydroxypropyl methacrylate, γ -hydroxypropyl acrylate, γ -hydroxypropyl methacrylate, 3-chloro-2-hydroxypropyl acrylate, 3-chloro-2-hydroxypropyl methacrylate, diethyleneglycol monoacrylic acid esters, diethyleneglycol monomethacrylic acid esters, glycerin monoacrylic acid esters, N-methylolacrylamide and N-methylolmethacrylamide), vinyl alcohol and its ethers (e.g., vinyl methyl ether, vinyl ethyl ether and vinyl propyl ether), esters of vinyl alcohol with a compound having a carboxyl group (i.e., vinyl acetate, vinyl propionate and vinyl butyrate); acrylic amides (e.g., acrylamide, methacrylamide and diacetoneacrylamide) and their methylol compounds, acid chlorides (e.g., acrylic acid chloride and methacrylic acid chloride), and monomers having a nitrogen atom or an alicyclic ring having a nitrogen atom (e.g., vinyl pyridine, vinyl pyrrolidone, vinyl imidazole and ethylene imine). In addition, polymers such as polyoxyethylene compounds (e.g., polyoxyethylene, polyoxypropylene, polyoxyethylenealkyl amines, polyoxypropylenealkyl amines, polyoxyethylenealkyl amides, polyoxypropylenealkyl amides, polyoxyethylene nonylphenyl ethers, polyoxyethylene laurylphenyl ethers, polyoxyethylene stearylphenyl esters, and polyoxyethylene nonylphenyl esters); and cellulose compounds such as methyl cellulose, hydroxyethyl cellulose and hydroxypropyl cellulose, can also be used as the polymeric protective colloid.

[0042]

When compounds such as calcium phosphate which are soluble in an acid or alkali are used as a dispersion stabilizer, the resultant toner particles are preferably mixed with an acid such as hydrochloric acid, followed by washing with water to remove calcium phosphate from the toner particles. In addition, calcium phosphate can be removed using a zymolytic method.

When a dispersant is used, the resultant particles are preferably washed after the particles are subjected to an elongation and/or a crosslinking reaction to impart good charge ability to the particles.

[0043]

When an aqueous dispersion or emulsion is prepared, a solvent which can dissolve the urea-modified polyester or prepolymer (A) used is preferably used because the resultant particles have a sharp particle diameter distribution. The solvent is preferably volatile and has a boiling point lower than 100 °C because of easily removed from the dispersion after the particles are formed. Specific examples of such a solvent include toluene, xylene, benzene, carbon tetrachloride, methylene chloride, 1,2-dichloroethane, 1,1,2-trichloroethane, trichloroethylene, chloroform, monochlorobenzene, dichloroethylidene, methyl acetate, ethyl acetate, methyl ethyl ketone, methyl isobutyl ketone, etc. These solvents can be used alone or in combination. Among these solvents, aromatic solvents such as toluene and xylene; and halogenated hydrocarbons such as methylene chloride, 1,2-dichloroethane, chloroform, and carbon tetrachloride are preferably used. The addition amount of such a solvent is from 0 to 300 parts by weight, preferably from 0 to 100 and more preferably from 25 to 70 parts by weight, per 100 parts by weight of the prepolymer (A) used. When such a solvent is used to prepare a particle dispersion, the solvent is removed upon application of heat thereto under a normal or reduced pressure after the particles are subjected to an extension treatment and/or a crosslinking treatment.

[0044]

When a urea-modified polyester (i) is synthesized using a prepolymer (A), an amine (B) may be added to an aqueous medium before or after a composition including the prepolymer (A) is added to the aqueous medium. In the latter case, the reaction is performed from the surface of the particles of the composition, whereby the content of the urea-modified polyester (i) is changed in the direct direction of the particles.

[0045]

The reaction time of extension and/or crosslinking is determined depending on the reacting property of the prepolymer (A) and the amine (B) used, but the reaction time is generally from 10 minutes to 40 hours, and preferably 2 hours to 24 hours. The reacting temperature is generally from 0 to 150°C and

preferably from 20 to 80°C. In addition, a known catalyst can optionally be used. Specific examples of the catalyst include dibutyltin laurate and dioctyltin laurate.

[0046]

In order to remove an organic solvent from the thus prepared emulsion, a method in which the emulsion is gradually heated to perfectly evaporate the organic solvent included in the drops of the oil phase liquid can be used. Alternatively, a method in which the emulsion is sprayed in a dry environment to dry the organic solvent in the drops of the oil phase liquid and water in the dispersion, resulting in formation of toner particles, can be used. Specific examples of such a dry environment include gases of air, nitrogen, carbon dioxide, combustion gas, etc., which are preferably heated to a temperature not lower than the boiling point of the solvent having the highest boiling point among the solvents used in the emulsion or dispersion. Toner particles having desired properties can be rapidly prepared by performing this treatment using a spray dryer, a belt dryer, a rotary kiln, or the like.

When the thus prepared toner particles have a wide particle diameter distribution even after the particles are subjected to a washing treatment and a drying treatment, the toner particles are preferably subjected to a classification treatment using a cyclone, a decanter or a method utilizing centrifuge to remove fine particles therefrom. However, it is preferable to perform the classification operation in the liquid having the particles in view of efficiency.

The thus prepared toner particles are then mixed with one or more other particulate materials such as charge controlling agents, fluidizers and colorants optionally upon application of mechanical impact thereto to fix the particulate materials on the toner particles.

Specific examples of such mechanical impact application methods include methods in which a mixture is mixed with a highly rotated blade and methods in which a mixture is put into a jet air to collide the particles against each other or a collision plate. Specific examples of such mechanical impact applicators include ONG MILL (manufactured by Hosokawa Micron Co., Ltd.), modified I TYPE MILL in which the pressure of air used for pulverizing is reduced (manufactured by Nippon Pneumatic Mfg. Co., Ltd.), HYBRIDIZATION SYSTEM (manufactured by Nara Machine Co., Ltd.), KRYPTON SYSTEM (manufactured by Kawasaki Heavy Industries, Ltd.), automatic mortars, etc.

[0047]

(Carrier for two-component developer)

The toner of the present invention can be used for a two-component developer in which the toner is mixed with a magnetic carrier. The weight ratio (T/C) of the toner (T) to

the carrier (C) is preferably from 1/100 to 10/100. Suitable carriers for use in the two component developer include known carrier materials such as iron powders, ferrite powders, magnetite powders, magnetic resin carriers, which have a particle diameter of from about 20 μm to about 200 μm . The surface of the carriers may be coated with a resin. Specific examples of such resins to be coated on the carriers include amino resins such as urea-formaldehyde resins, melamine resins, benzoguanamine resins, urea resins, and polyamide resins, and epoxy resins. In addition, vinyl or vinylidene resins such as acrylic resins, polymethylmethacrylate resins, polyacrylonitrile resins, polyvinyl acetate resins, polyvinyl alcohol resins, polyvinyl butyral resins, polystyrene resins, styrene-acrylic copolymers, halogenated olefin resins such as polyvinyl chloride resins, polyester resins such as polyethyleneterephthalate resins and polybutyleneterephthalate resins, polycarbonate resins, polyethylene resins, polyvinyl fluoride resins, polyvinylidene fluoride resins, polytrifluoroethylene resins, polyhexafluoropropylene resins, vinylidene fluoride-acrylate copolymers, vinylidene fluoride-vinyl fluoride copolymers, copolymers of tetrafluoroethylene, vinylidene fluoride and other monomers including no fluorine atom, and silicone resins.

If desired, an electroconductive powder may be included in the coating layer. Specific examples of such electroconductive powders include metal powders, carbon blacks, titanium oxide, tin oxide, and zinc oxide. The average particle diameter of such electroconductive powders is preferably not greater than 1 μm . When the particle diameter is larger than 1 μm , it is hard to control the resistance of the coating layer.

The toner of the present invention can also be used as a one-component magnetic developer or a one-component non-magnetic developer, which does not use a carrier.

[0048]

[Embodiments]

Hereinafter, embodiments of the present invention will now be described. The present invention is, however, not limited thereto. In the following description, a part shows a weight part.

<Synthesis of particulate resin emulsion>

Manufacturing Example 1

The following components were contained in a reaction container having a stirrer and a thermometer and agitated for 15 minutes by a stirrer at a speed of 400 rpm to prepare a white emulsion.

Deionized water

683 parts

Sodium salt of sulfate of ethylene oxide adduct of methacrylic acid (ELEMNOL RS-30, manufactured by Sanyo

Chemical Industries, Ltd.)	11 parts
Styrene	83 parts
Methacrylic acid	83 parts
Butyl acrylate	110 parts
Ammonium	1 part

The emulsion was heated to 80 °C to perform a reaction for 5 hours. Further, 30 parts of a 1 % aqueous solution of ammonium persulfate were added thereto drop by drop and the mixture was aged for 5 hours to prepare an aqueous dispersion of a vinyl resin (styrene-methacrylic acid-butyl acrylate-sodium salt of sulfate of ethylene oxide adduct of methacrylic acid copolymer). The volume average particle diameter of the thus prepared fine particle dispersion (1) was 0.09 μm when measured with a particle diameter measuring instrument LA-920 manufactured by Horiba Ltd. A part of the fine particle dispersion (1) was dried to isolate the resin component. The glass transition temperature (T_g) of the resin component was 58 °C.

[0049]

Manufacturing Example 2

The procedure for preparation of the fine particle dispersion (1) in Manufacturing Example 1 was repeated except that 1 part of a crosslinking agent, divinyl benzene, was mixed with the components in the reaction container. Thus, a fine particle dispersion (2) was prepared. The volume average particle diameter of the fine particle dispersion (2) was 0.10 μm , and the glass transition temperature (T_g) of the resin component was 78 °C.

[0050]

Manufacturing Example 3

The procedure for preparation of the fine particle dispersion (1) in Manufacturing Example 1 was repeated except that 110 parts of butyl acrylate were not added and the addition amount of each of styrene and methacrylic acid was changed to 138 parts. Thus, a fine particle dispersion (3) was prepared. The volume average particle diameter of the fine particle dispersion (3) was 0.11 μm , and the glass transition temperature (T_g) of the resin component in the fine particle dispersion (3) was 150 °C.

[0051]

<Preparation of aqueous phase liquid>

Manufacturing Example 4

1000 parts of deionized water, 83 parts of fine particle dispersion (1), 37 parts of aqueous solution of sodium salt of dodecyl diphenyl ether disulfonic acid with solid content of 48.5% (ELEMNOL MON-7, manufactured by Sanyo Chemical Industries, Ltd.) and 90 parts of Ethyl acetate are mixed while agitated to prepare a milk-white liquid. This is an aqueous phase liquid (1).

[0052]

Manufacturing Example 5

1000 parts of deionized water, 83 parts of fine particle dispersion (2), 37 parts of aqueous solution of sodium salt of dodecyl diphenyl ether disulfonic acid with solid content of 48.5% (ELEMNOL MON-7, manufactured by Sanyo Chemical Industries, Ltd.) and 90 parts of Ethyl acetate are mixed while agitated to prepare a milk-white liquid. This is an aqueous phase liquid (2).

[0053]

Manufacturing Example 6

1000 parts of deionized water, 3 parts of particulate silica (AEROSIL 130, manufactured by Nippon Aerosil Co., average primary particle diameter of about 16 nm), 37 parts of aqueous solution of 48.5% sodium salt of dodecyl diphenyl ether disulfonic acid (ELEMNOL MON-7, manufactured by Sanyo Chemical Industries, Ltd.), 90 parts of ethyl acetate were mixed while agitated to obtain a milk-white liquid. This is an aqueous phase liquid (3).

[0054]

Manufacturing Example 7

1000 parts of deionized water, 4 parts of particulate titanium dioxide (P-25, manufactured by Nippon Aerosil Co., average primary particle diameter of about 21 nm), 37 parts of aqueous solution of 48.5% sodium salt of dodecyl diphenyl ether disulfonic acid (ELEMNOL MON-7, manufactured by Sanyo Chemical Industries, Ltd.) and 90 parts of ethyl acetate were mixed while agitated to prepare a milk-white liquid. This is an aqueous phase liquid (4).

[0055]

Manufacturing Example 8

1000 parts of deionized water, 45 parts of fine particle dispersion (1), 2 parts of particulate titanium dioxide (P-25, manufactured by Nippon Aerosil Co., average primary particle diameter of about 21 nm), 37 parts of aqueous solution of 48.5% sodium salt of dodecyl diphenyl ether disulfonic acid (ELEMNOL MON-7, manufactured by Sanyo Chemical Industries Ltd.) and 90 parts of ethyl acetate were mixed while agitated to prepare a milk-white liquid. This is an aqueous phase liquid (5).

[0056]

Manufacturing Example 9

1000 parts of deionized water, 83 parts of fine particle dispersion (3), 37 parts of aqueous solution of 48.5% sodium salt of dodecyl diphenyl ether disulfonic acid (ELEMNOL MON-7, manufactured by Sanyo Chemical Industries Ltd), and 90 parts of ethyl acetate were mixed while agitated to prepare a milk-white liquid. This is an aqueous phase liquid (6).

[0057]

Manufacturing Example 10

1000 parts of deionized water, 40 parts of aqueous solution of 48.5 % sodium salt of dodecyl diphenyl ether disulfonic acid (ELEMNOL MON-7, manufactured by Sanyo Chemical Industries Ltd.) and 90 parts of ethyl acetate were mixed while agitated to prepare a liquid no including fine particles. This is an aqueous phase liquid (7).

[0058]

<Synthesis of polyester resin with a relatively low molecular weight>

Manufacturing Example 11

The following components were contained in a reaction container having a condenser tube, a stirrer and a nitrogen introducing tube and reacted for 8 hours at 230°C under normal pressure.

Adduct of 2 mole of ethylene oxide with bisphenol A	229 parts;
Adduct of 3 mole of propylene oxide with bisphenol A	529 parts;
Terephthalic acid	208 parts;
Adipic acid	46 parts; and
Dibutyl tin oxide	2 parts

The reacted components were further reacted for 5 hours under a reduced pressure of from 10 to 15 mmHg. Thereafter, 44 parts of trimellitic anhydride were added thereto to perform a reaction for 2 hours at 180°C under a normal pressure. Thus, a polyester (1) having a relatively low molecular weight was prepared. The low molecular weight polyester (1) has a number average molecular weight of 2500, a weight average molecular weight of 6700, a Tg of 43 °C, and an acid value of 25 mgKOH/g.

[0059]

Manufacturing Example 12

The following components were contained in a reaction container having a condenser, a stirrer and a nitrogen introducing tube and reacted for 8 hours at 230 °C under a normal pressure.

Adduct of 2 mole of ethylene oxide with bisphenol A	262 parts;
Adduct of 2 mole of propylene oxide with bisphenol A	220 parts;
Adduct of 3 mole of propylene oxide with bisphenol A	236 parts;
Terephthalic acid	266 parts;
Adipic acid	48 parts; and
Dibutyl tin oxide	2 parts

The reacted components were further continued for 5 hours under a reduced pressure of from 10 to 15 mmHg. Further, 34 parts of trimellitic anhydride were added thereto to perform a reaction for 2 hours at 180 °C under a normal pressure. Thus, a low molecular weight polyester (2) was prepared. The low molecular weight polyester (2) has a number average molecular weight of 2390, a weight average molecular weight of 6010, a Tg of 62 °C, and an acid value of 20.7 mgKOH/g.

[0060]

<Synthesis of prepolymer having isocyanate group>

Manufacturing Example 13

The following components were contained in a reaction container having a condenser, a stirrer and a nitrogen introducing tube and reacted for 8 hours at 230°C under a normal pressure.

Adduct of 2 mole of ethylene oxide with bisphenol A 682 parts;

Adduct of 2 mole of propylene oxide with bisphenol A 81 parts;

Terephthalic acid 283 parts;

Trimellitic anhydride 22 parts; and

Dibutyl tin oxide 2 parts

Then the reaction was further continued for 5 hours under a reduced pressure of from 10 to 15 mmHg. Thus, an intermediate polyester (1) was prepared. The intermediate polyester (1) has a number average molecular weight of 2100, a weight average molecular weight of 9500, a Tg of 55°C, an acid value of 0.5 mgKOH/g and a hydroxyl value of 51 mgKOH/g.

Then the following components were contained in a reaction container having a condenser tube, a stirrer and a nitrogen introducing tube and reacted for 5 hours at 100 °C to prepare a prepolymer (1).

The intermediate polyester (1) 410 parts;

Isophorone diisocyanate 89 parts; and

Ethyl acetate 500 parts

The prepolymer (1) includes free isocyanate in an amount of 1.53 % by weight.

[0061]

<Preparation of ketimine compound>

Manufacturing Example 14

In a reaction container having a stirrer and a thermometer, 170 parts of isophorone diamine and 75 parts of methyl ethyl ketone were contained and reacted for 5 hours at 50 °C to prepare a ketimine compound (1). The ketimine compound (1) had an amine value of 418 mgKOH/g.

[0062]

<Preparation of dye master batch>

Manufacturing Example 15

1200 parts of water, 540 parts of carbon black (PRINTEX 60, manufactured by Degussa A.G.), and 1200 parts of low molecular weight polyester (1) were mixed with a Henschel mixer. The mixture was kneaded for 45 minutes at 130 °C by a two-roll mill and crushed by a pulverizer after cooling, to prepare a master batch (1) having a particle diameter of 1 mm.

[0063]

Hereinafter, an evaluation method and evaluation conditions will be explained.

Particle diameter of toner

The particle diameter (i.e., volume average particle

diameter and number average particle diameter) of toner was measured with a particle diameter measuring instrument, COULTER COUNTER TA II, manufactured by Coulter Electronics, Inc., which is equipped with an aperture having a diameter of 100 μm .

[0064]

(2) Fixability

(a) Each developer was set in a copier, IMAGIO NEO 450, which can produce 45 copies of A4 size per minute, and black solid images were continuously produced on a plain paper (TYPE 6200 paper from Ricoh Co., Ltd.) and a thick paper (COPY/PRINT PAPER 135 from NBS Ricoh) while the developing conditions were controlled such that the weight of the solid toner image is $1.0 \pm 0.1 \text{ mg/cm}^2$. In addition, the temperature of the fixing roller was changed to determine the offset temperature (when the plain paper was used) and the minimum fixable temperature (when the thick paper was used). The minimum fixable temperature was defined as the lowest fixing temperature of the fixing roller in a fixing temperature range in which when a fixed image was rubbed with a pad, the image has an image density not lower than 70 % of the original image density.

(b) The procedure for evaluation in paragraph (a) was repeated except that the fixing device of IMAGIO NEO 450 was replaced with the fixing device illustrated in Fig. 2.

In this case, the fixing belt (B) includes a polyimide substrate having a thickness of 100 μm ; an intermediate elastic layer which is located on the substrate and is made of a silicone rubber and which has a thickness of 100 μm ; and an offset preventing layer which is located as an outermost layer and is made of a perfluoroalkoxyethylene copolymer (PFA) and which has a thickness of 15 μm . The fixing roller R1 is made of a foamed silicone resin. The pressure roller R2 includes a metal cylinder which is made of a stainless steel (SUS) and has a thickness of 1 mm; and an offset preventing layer which is a combination of a PFA tube; and a silicone rubber layer and which has a thickness of 2 mm. The heat roller R3 is made of an aluminum cylinder having a thickness of 2 mm, and the pressure of the heat roller R3 applied to the fixing belt (B) is $1 \times 10^5 \text{ Pa}$.

[0065]

(3) Transferability

Images were produced in the same way as performed in the evaluation of the fixability. When toner image formed on the photoreceptor was transferred to a receiving material, the copier was suddenly turned off to visually determine the amount of toner remaining on an area of the photoreceptor, from which toner image had been transferred to the receiving material.

The transferability of the toner is classified into the following four grades:

©: The amount of residual toner is very little, i.e., the

toner has excellent transferability.

○: The amount of residual toner is little, i.e., the toner has good transferability.

△: The toner has a transferability almost the same as those of conventional toner.

X: The amount of residual toner is very large, i.e., the toner has poor transferability.

[0066]

(4) Preservability

Ten (10) grams of toner was contained in a container of 30 ml. The container was tapped 150 times to condense the toner. The container including the toner was preserved for 24 hours in a chamber in which the temperature was controlled at 50 °C. Then the container was cooled to room temperature. The toner was sifted using a screen having openings of 74 μm, and the weight of the toner remaining on the screen was measured. The preservability of the toner is classified into the following four grades:

◎: There is no toner remaining on the screen.

○: The weight of the toner remaining on the screen is less than 1 g.

△: The weight of the toner remaining on the screen is not less than 1 g and less than 4 g.

X: The weight of the toner remaining on the screen is not less than 4 g.

[0067]

Example 1

<Preparation of oil phase liquid>

The following components were contained in a reaction container having a stirrer and a thermometer.

Low molecular polyester (1) 378 parts

Synthesized ester wax 110 parts

Charge controlling agent 22 parts

(Salicylic metal complex E-84, manufactured by Orient Chemical Industries Ltd.)

Ethyl acetate 947 parts

The mixture was heated to 80 °C while agitated. After the mixture was agitated at 80 °C for 5 hours, followed by cooling to 30 °C in an hour.

Next, 500 parts of the master batch (1) and 500 parts of ethyl acetate were added thereto and the mixture was mixed for 1 hour to prepare a material solution (1).

The material solution (1) of 1,324 parts was transferred to a container and was subjected to a dispersion treatment using a bead mill (ULTRA VISCO MILL, manufactured by Aimex Co., Ltd.) under the following condition.

Liquid feeding speed: 1 kg/hour

Disc rotating speed: 6 m/second

Beads: zirconia beads having a size of 0.5 mm were contained in the mill in an amount of 80 % by volume based on the volume of the vessel

Number of times of dispersion: 3 passes

Next, 1324 parts of a 65 % ethyl acetate solution of the low molecular polyester (1) were added thereto and the mixture was passed once through the bead mill under the above-mentioned conditions to prepare a pigment/wax dispersion (1). The solid content of the pigment/wax dispersion (1) was 50 % when measured by heating the dispersion at 130 °C for 30 minutes.

[0068]

<Emulsification and removal of solvent>

The following components were contained in a container.

Pigment/wax dispersion (1) 650 parts

Prepolymer (1) 140 parts

Ketimine compound (1) 6 parts

The components were mixed by a TK HOMOMIXER (manufactured by Tokushu Kika Kogyo Co., Ltd.) at a speed of 5,000 rpm for 1 minute.

Then 1,200 parts of the aqueous phase (1) were added thereto to be mixed by the TK HOMOMIXER at a speed of 13,000 rpm for 20 minutes to prepare an emulsion slurry (1).

The emulsion slurry (1) was contained in a container having a stirrer and a thermometer to be subjected to a solvent removing treatment at 30 °C for 8 hours, followed by aging at 40 °C for 8 hours to prepare a dispersion slurry (1).

[0069]

<Washing and drying>

The dispersion slurry (1) of 100 parts was filtered under a reduced pressure. Then the following operations were performed to prepare a filter cake (1).

(1) 100 parts of ion-exchanged water were added to the cake obtained by filtering the dispersion slurry (1) and the mixture was mixed for 10 minutes by a TK HOMOMIXER at a speed of 12,000 rpm, followed by filtering to prepare a filtered cake (a).

(2) 100 parts of a 10 % aqueous solution of sodium hydroxide were added to the filtered cake (a) and the mixture was mixed for 30 minutes by the TK HOMOMIXER at a speed of 12,000 rpm while applying ultrasonic vibration, followed by filtering under a reduced pressure. This ultrasonic alkali washing was repeated twice to prepare a filtered cake (b).

(3) 100 parts of a 10 % aqueous solution of hydrochloric acid were added to the filter cake (b) and the mixture was mixed for 10 minutes by the TK HOMOMIXER at a speed of 12,000 rpm, followed by filtering to prepare a filtered cake (c).

(4) 300 parts of ion-exchanged water were added to the filtered cake (c) and the mixture was mixed for 10 minutes by

the TK HOMO MIXER at a speed of 12,000 rpm, followed by filtering. This operation was performed twice to prepare the filtered cake (1).

The filter cake (1) was dried by an air dryer at 45 °C for 48 hours, followed by sifting with a screen having 75 μm openings to prepare toner (1) (i.e., toner particles).

The photographs of particles of the toner (1) taken by a scanning electron microscope are shown in Figs. 1(a) through 1(c). The photograph in Fig. 1(a) was taken with a magnification of 2,000. The photograph in Fig. 1(b) was taken with a magnification of 13,000, in which a part of Fig. 1(a) is enlarged. The photograph in Fig. 1(c) was taken with a magnification of 50,000. As can be understood especially from Fig. 1(b) and 1(c), a fine particulate vinyl resin is present on the surface of the toner particles while embedded thereto.

The toner (1) has a volume average particle diameter of 5.43 μm , and a Tg of 46 °C. In addition, the content of the THF-insoluble components in the binder resin of the toner (1) was 12 %. Five (5) parts of the toner was mixed with 95 parts of a carrier which had been prepared by coating a magnetite powder having an average particle diameter of 35 μm with a coating liquid including the following components to prepare a developer.

Methyl methacrylate resin	35 parts
Silicone resin	60 parts
Carbon black (KETJEN BLACK)	5 parts

The thus prepared developer was subjected to an image forming test to evaluate the fixability, offset resistance, transferability and preservability of the toner. The evaluation methods are described below. With respect to the fixability, the evaluation method (a) was used for the toner prepared in Examples 1 to 5; and the evaluation method (b) was used for the toner prepared in Example 5.

The results are shown in Table 1. As a result, the toner (1) had a good combination of low temperature fixability, offset resistance, preservability and transferability.

[0070]

Example 2

The procedure for preparation and evaluation of the toner (1) in Example 1 was repeated except that the aqueous phase liquid (1) was replaced with the aqueous phase liquid (3) that includes a silica.

The thus prepared toner had a volume average particle diameter of 4.76 μm , and a Tg of 48 °C. In addition, the content of the THF-insoluble components of the binder resin in the toner was 11 %.

As can be understood from the results as shown in Table 1, the toner has a good combination of low temperature fixability, offset resistance, preservability and transferability.

[0071]

Example 3)

The procedure for preparation and evaluation of the toner (1) in Example 1 was repeated except that the aqueous phase liquid (1) was replaced with the aqueous phase liquid (4) that includes a titanium dioxide.

The thus prepared toner had a volume average particle diameter of 5.14 μm , and a Tg of 47 °C. In addition, the content of the THF-insoluble components of the binder resin in the toner was 12 %.

As can be understood from the results as shown in Table 1, the toner has a good combination of low temperature fixability, offset resistance, preservability and transferability.

[0072]

Example 4

The procedure for preparation and evaluation of the toner (1) in Example 1 was repeated except that the aqueous phase liquid (1) was replaced with the aqueous phase liquid (5) that includes a particulate resin and a titanium dioxide.

The thus prepared toner had a volume average particle diameter of 5.22 μm , and a Tg of 47 °C. In addition, the content of the THF-insoluble components of the binder resin in the toner was 12 %.

As can be understood from the results as shown in Table 1, the toner has a good combination of low temperature fixability, offset resistance, preservability and transferability.

[0073]

Example 5

The procedure for preparation and evaluation of the toner (1) in Example 1 was repeated except that the aqueous phase liquid (1) was replaced with the aqueous phase liquid (2) that includes a particulate resin.

The thus prepared toner had a volume average particle diameter of 5.51 μm , and a Tg of 48 °C. In addition, the content of the THF-insoluble components of the binder resin in the toner was 12 %.

As can be understood from the results as shown in Table 1, the toner has a good combination of low temperature fixability, offset resistance, preservability and transferability. In particular, the toner has excellent low temperature fixability, offset resistance and preservability.

[0074]

Example 6

The procedure for preparation and evaluation of the toner in Example 5 was repeated except that the method (b) was used for evaluating the fixability of the toner.

Since the toner has good low temperature fixability so that the fixing temperature can be decreased and in addition

temperature rising time can be reduced, whereby fixing energy can be dramatically saved. °C

[0075]

Comparative Example 1

The procedure for preparation and evaluation of the toner (1) in Example 1 was repeated except that the aqueous phase liquid (1) was replaced with the aqueous phase liquid (7) that includes no particulate resin.

The thus prepared toner had a volume average particle diameter of 6.85 μm , and a Tg of 45 °C. In addition, the content of the THF-insoluble components of the binder resin in the toner was 13 %.

As can be understood from the results as shown in Table 1, the toner has a good low temperature fixability, but the toner has poor offset resistance, preservability and transferability.

[0076]

Comparative Example 2

The procedure for preparation and evaluation of the toner (1) in Example 1 was repeated except that the aqueous phase liquid (1) was replaced with the aqueous phase liquid (6) that includes a particulate resin having a Tg of 150 °C.

The thus prepared toner had a volume average particle diameter of 5.43 μm , and a Tg of 49 °C. In addition, the content of the THF-insoluble components of the binder resin in the toner was 11 %.

As can be understood from the results as shown in Table 1, the toner has a good preservability, but the toner has a high minimum fixing temperature (i.e., has a poor fixability).

[0077]

Comparative Example 3

The procedure for preparation and evaluation of the toner (1) in Example 1 was repeated except that the low molecular polyester (1) was replaced with the low molecular polyester (2) having a Tg of 62 °C.

The thus prepared toner had a volume average particle diameter of 5.81 μm , and a Tg of 61.3 °C. In addition, the content of the THF-insoluble components of the binder resin of the toner was 12 %.

As can be understood from the results as shown in Table 1, the toner has a good preservability, but the toner has a high minimum fixing temperature (i.e., has a poor fixability).

[0078]

Comparative Example 4

The procedure for preparation and evaluation of the toner (1) in Example 1 was repeated except that when the emulsion slurry was prepared, the prepolymer (1) and the ketimine compound were replaced with 146 parts of the low molecular polyester (1).

The thus prepared toner had a volume average particle

diameter of 3.78 μm , and a Tg of 44.2 $^{\circ}\text{C}$. In addition, the content of the THF-insoluble components of the binder resin of the toner was 0 %.

As can be understood from the results as shown in Table 1, the toner has good low temperature fixability, but the toner has a slightly poor offset resistance. In addition, the preservability and transferability of the toner were slightly deteriorated.

[0079]

Comparative Example 5

The procedure for preparation and evaluation of the toner (1) in Example 1 was repeated except that when the emulsion slurry was prepared, the addition amounts of the pigment/wax dispersion (1), the prepolymer (1) and the ketimine compound (1) were changed to 800 parts, 280 parts and 12.0 parts, respectively.

The thus prepared toner had a volume average particle diameter of 6.39 μm , and a Tg of 49.4 $^{\circ}\text{C}$. In addition, the content of the THF-insoluble components of the binder resin in the toner was 23 %.

As can be understood from the results as shown in Table 1, the toner has an excellent offset resistance, but the toner has poor low temperature fixability.

[0080]

Table 1

	Minimum fixable temperature ($^{\circ}\text{C}$)	Hot offset temperature ($^{\circ}\text{C}$)	Preserv- ability	Transfer- ability
Ex. 1	135	230	○	○
Ex. 2	135	235	○	○
Ex. 3	135	235	○	○
Ex. 4	135	230	○	○
Ex. 5	125	Not lower than 240	⊙	○
Ex. 6	110	230	⊙	○
Comp. Ex. 1	120	180	X	X
Comp. Ex. 2	155	240	⊙	○
Comp. Ex. 3	150	240	⊙	○
Comp. Ex. 4	125	160	△	△
Comp. Ex. 5	160	Not lower than 240	○	○

[0081]

[Effects of the Invention]

As is clear from the detailed explanation, according to the present invention, color toner and developer, excellent in a low temperature fixing property and having a satisfactory offset preventive capability without applying release oil to the fixing

roller or by applying a small quantity of oil, and an optimal storage property and transferability, may be provided and a fixing method using such toner excellent in the low temperature fixing property and the offset preventive capability may also be provided. When the fixing operation is performed using the toner of the present invention, and using a belt heat and fixing method having a long fixing duration (i.e., nip period), a further lower temperature fixing operation may be enabled.

[Brief Description of the Drawing]

[Fig. 1]

Figs. 1(a), 1(b) and 1(c) are photographs of toner taken with a scanning electron microscope.

[Fig. 2]

Fig. 2 is an explanatory view of a belt fixing apparatus.

[Reference numerals]

R1	Fixing roller
R2	Pressurizing roller
R3	Heat roller
R4	Cleaning roller
B	Fixing belt
P	Pressurizing spring
G	Guide
H	Heat source